Methyl Cation Affinities of Rare Gases and Nitrogen and the Heat of Formation of Diazomethane

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The methyl cation affinities of the rare gases have been calculated at 0 and 298 K by using coupled cluster theory including noniterative, quasiperturbative triple excitations with the new correlation-consistent basis sets for Xe up through aug-cc-pV5Z in some cases. To achieve near chemical accuracy (±1 kcal/mol) in the thermodynamic properties, we add to the estimated complete basis set valence binding energies, based on frozen core coupled cluster theory energies, two corrections: (1) a core/valence correction and (2) a scalar relativistic correction. Vibrational zero-point energies were computed at the coupled cluster level of theory at the CCSD(T)/aug-cc-pVDZ level. The calculated rare gas methyl cation affinities (MCA in kcal/mol) at 298 K are the following: MCA(He) = 1.7, MCA(Ne) = 2.5, MCA(Ar) = 16.9, MCA(Kr) = 25.5, and MCA(Xe) = 36.6. Because of the importance of the MCA(N_2) in the experimental measurements of the MCA scale, we calculated a number of quantities associated with $CH_3N_2^+$ and CH_2N_2. The calculated values for diazomethane at 298 K are: $\Delta H_f(CH_2N_2)$ = 65.3 kcal/mol, PA(CH_2N_2) = 211.9 kcal/mol, and MCA(N_2) = 43.2 kcal/mol.

Introduction

Beginning with the work of Bartlett,[1] scientists have been intrigued by the possibility of rare gas compounds. A variety of compounds with covalent bonds have been synthesized.[2−9] Chemists have been studying the chemistry of charged Xe compounds in both the gas phase and the solid state and $XeCH_3^+$ was first observed in an ion cyclotron resonance spectrometer in 1971.[10] More recently McMahon and Hovey measured the C−Xe bond strength in $XeCH_3^+$ as 55.2 ± 2.5 kcal/mol[11] and that of C−Kr in $KrCH_3^+$ as 47.7 ± 2.5 kcal/mol[12] by using ICR and pulsed high-pressure mass spectrometric techniques. These values were revised downward based on a revision of the methyl cation affinity (MCA) of N_2 to values of 39.7 and 46.6 kcal/mol for Kr and Xe, respectively.[13] Hiraoka and co-workers have measured the bond energy of $ArCH_3^+$ as 11.3 kcal/mol[14] and have recently reported values of 1.2 ± 0.3 and 19.8 ± 2.0 kcal/mol for the MCA of Ne and Kr, respectively, based on clustering reactions in a high-pressure mass spectrometer.[15] In addition, they showed that the MCA of Xe is 2.0 kcal/mol higher than that of N_2 based on an exchange reaction. There have been a number of other studies of rare gas methyl cation complexes. Dopfer and co-workers have used infrared photodissociation measurements with MP2/aug-cc-pVTZ calculations to probe the structure of CH_3^+−Rg for Rg = He, Ne, and Ar.[16−19] These authors calculate D_e values of 2.02 kcal/mol (707 cm^{-1}) for Rg = He, 2.74 kcal/mol (958 cm^{-1}) for Rg = Ne, and 18.3 kcal/mol (6411 cm^{-1}) for Rg = Ar. Hiraoka and co-workers[15] report calculated MCA's of 0.6, 2.2, 15.9, and 24.1 kcal for Rg = He, Ne, Ar, and Kr, respectively, at the QCISD-(T)(full)/6-311++G(2df,p) level at the B3LYP/6-311++G(d,p) level and the MCA of Xe is calculated to be 39.0 kcal/mol at the B3LYP/DZVP level.

We now have the ability to theoretically model the thermochemistry of the rare gas compounds using an approach to the prediction of the thermodynamic properties of molecules based on molecular orbital theory that we have been developing.[20] The calculations start with a systematic sequence of extended basis set, frozen core CCSD(T)(FC) calculations[21] that approach the complete basis set (CBS) limit. The resulting total energies are extrapolated to the CBS limit in an attempt to eliminate basis set truncation error. They are further adjusted to include core-valence correlation, molecular scalar relativistic corrections, and atomic spin−orbit corrections.[20] Finally, one must include a correction for zero-point vibrational energies, ZPE's, to obtain

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zero-point inclusive atomization energies, $\sum D_0$. Given $\sum D_0$ and the heats of formation of the elements, we can then calculate the heat for formation of a given compound. Our composite, nonparametrized approach implicitly assumes that the effects of the smaller corrections are additive to the extrapolated CBS energies which only account for valence correlation effects. In general, this composite CCSD(T) approach is capable of achieving near chemical accuracy, i.e., ±1 kcal/mol, with respect to experiment, in thermochemical calculations for chemical systems composed of first and second row elements, as documented for nearly 300 compounds in the Environmental and Molecular Sciences Laboratory Computational Results Database.[22] For example, we have recently applied this approach to the prediction of the binding energies and heats of formation of a number of small halogenated compounds including IF and found excellent agreement with reliable experimental values.[23] These methods have also been applied to the prediction of the heats of formation of the xenon fluorides.[24]

For this approach to work, one must have a reliable sequence of basis sets that extrapolate to the complete basis set limit. These basis sets were initially only available for 1st, 2nd, and 3rd row main group elements.[25] Recently, Peterson and co-workers have developed such basis sets[26] in combination with effective core potentials from the Stuttgart group for all of the main group atoms thereby opening up these compounds to reliable calculations. We have used this approach to calculate the methyl cation affinities of the rare gases: He, Ne, Ar, Kr, and Xe. For comparison purposes, we note that the calculated proton affinities of the rare gases are in excellent agreement with experiment.[26]

Because of the importance of the methyl cation affinity of N_2 in the experimental MCA scale,[27] we have also calculated this value. The compound $CH_3N_2^+$ is, of course, protonated diazomethane so we have also calculated the proton affinity of diazomethane as well as its heat of formation. The proton affinity of CH_2N_2 has been under some dispute and our calculation will help to resolve this issue.[13] The heat of formation of diazomethane has long been of interest to kineticists because of its importance in the production of methylene (CH_2) by photolysis of diazomethane for use in chemical activation studies.[28] Surprisingly, its heat of formation is not well established from experiment.[29] The heat of formation of CH_2N_2 has been calculated at the G2 level.[30]

Computational Methods

In most CCSD(T) calculations of atomization energies, heats of formation, or bond dissociation energies, the largest source of error typically arises from the finite basis set approximation unless there is significant multireference character to the wave function. Our composite approach makes use of the systematic convergence properties of the valence correlation consistent family of basis sets including additional diffuse functions. These basis sets are conventionally denoted aug-cc-pVnZ, $n = \mathrm{D} - 5$ for the atoms for which they are available. For He, Ne, Ar C, N, and H, the standard aug-cc-pVnZ basis sets were used.[25] For heavier elements, we need to include the effects of relativity in the basis sets.[26] For Xe, a small core relativistic effective core potential (RECP) was used. The RECP subsumes the ($1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, and $3d^{10}$) orbital space into the 28-electron core set, leaving the ($4s^2$, $4p^6$, $5s^2$, $4d^{10}$, and $5p^6$) space with 26 electrons to be handled explicitly. Of the latter, only the ($5s^2$, $5p^6$) are active in our valence correlation treatment. For Kr, a similar basis set was used with the ($1s^2$, $2s^2$, $2p^6$) electrons in the core and 26 electrons are handled explicitly. The correlation consistent basis sets developed using relativistic pseudopotentials are labeled as aug-cc-pVnZ-PP. We use the shorthand notation of aVnZ to denote the combination of the aug-cc-pVnZ basis set on all atoms besides Xe and Kr and the aug-cc-pVnZ-PP basis set on Xe and Kr. Only the spherical component subset (e.g., 5-term d functions, 7-term f functions, etc.) of the Cartesian polarization functions were used. All CCSD(T) calculations were performed with either the MOLPRO-2002[31] program system on a single processor of an SGI Origin computer or with NWChem[32] and MOLPRO on the massively parallel HP Linux cluster in the Molecular Science Computing Facility in the William R. Wiley Environmental Molecular Sciences Laboratory.

The slow convergence of one-electron functions (basis set) to the CBS limit means that the remaining basis set truncation error remains unacceptably large if accuracy on the order of ±1 kcal/mol is desired. By exploiting the systematic convergence properties of the correlation consistent basis sets, it is possible to obtain reasonably accurate estimates of the CBS limit without having to resort to such extremely large basis sets that would unavoidably limit the use of our composite approach to small diatomic molecules. In previous work, we based our CBS estimates on one or more of the following formulas: a mixed exponential/Gaussian function of the form[33]

$$E(n) = E_{\mathrm{CBS}} + b\exp[-(n-1)] + c\exp[-(n-1)^2] \qquad (1)$$

where $n = 2$(aVDZ), 3(aVTZ), 4(aVQZ); a simple exponential function[34]

$$E(n) = E_{\mathrm{CBS}} + b\exp(-cx) \qquad (2)$$

or a formula that involves the reciprocal of $l_{\max}$[35]

$$E(l_{\max}) = E_{\mathrm{CBS}} + B/l_{\max}{}^3 \qquad (3)$$

The latter formula is formally to be applied to the correlation component of the total energy only, with the HF component extrapolated separately or taken from the largest basis set value. In practice, the effect on energy differences of treating the HF component separately or extrapolating the total energy is small. Experience has shown that the “best” extrapolation formula varies with the level of basis set and the molecular system and there is no universally agreed upon definition of best. Equations 1 and 2 are based on the observed convergence pattern displayed by the double- through quadruple-ζ correlation consistent basis sets. In a large number of comparisons of computed and experimental atomization energies, eq 1 was statistically slightly superior to the version of eq 3 when the largest basis sets were of quadruple-ζ quality.[20] Both of these expressions, in turn, were better than eq 2, the simple exponential fit. Equation 3 and similar expressions involving $1/l_{\max}$ are best suited for basis sets beyond quadruple-ζ, since they are motivated by the $1/Z$ perturbation theory work of Schwartz who dealt with 2-electron systems in the case where each angular momentum space was saturated.[36] The spread in CBS estimates can serve as a crude measure of the uncertainty in the CBS extrapolation. We use eq 3 to obtain CBS estimates of the total energy for the calculations with the 5-ζ level and eq 1 for molecules where the largest basis set was aug-cc-pVQZ.

Most electronic structure calculations invoke the frozen core approximation in which the energetically lower lying orbitals, e.g., the 1s in carbon, are excluded from the correlation treatment. To achieve atomization energies within ±1 kcal/mol of experiment, it is necessary to account for core-valence (e.g., intershell $1s^2 - 2s^22p^2$ in C) correlation energy effects. Core-

TABLE 1: Total Energies (E_h) for Rare Gas Methyl Cation Affinities[a]

molecule	basis set	energy	molecule	basis set	energy	molecule	basis set	energy
CH_3^+	aVDZ	−39.371002	Kr	aVDZ	−462.319290	$ArCH_3^+$	aVDZ	−566.364114
	aVTZ	−39.405712		aVTZ	−462.396565		aVTZ	−566.484233
	aVQZ	−39.414480		aVQZ	−462.419593		aVQZ	−566.518960
	aV5Z	−39.417023		aV5Z	−462.426999		aV5Z	−566.530052
	CBS(eq 3)	−39.419691		CBS(eq 3)	−462.434769		CBS(eq 3)	−566.541688
	CBS(eq 1)	−39.419203		CBS(eq 1)	−462.432483		CBS(eq 1)	−566.538275
He	aVDZ	−2.889548	Xe	aVDZ	−328.437108	$KrCH_3^+$	aVDZ	−501.727900
	aVTZ	−2.900598		aVTZ	−328.497639		aVTZ	−501.846726
	aVQZ	−2.902534		aVQZ	−328.521010		aVQZ	−501.877674
	aV5Z	−2.903201		aV5Z	−328.527757		aV5Z	−501.887609
	CBS(eq 3)	−2.903901		CBS(eq 3)	−328.534836		CBS(eq 3)	−501.898033
	CBS(eq 1)	−2.903458		CBS(eq 1)	−328.534716		CBS(eq 1)	−501.894476
Ne	aVDZ	−128.709295	$HeCH_3^+$	aVDZ	−42.263296	$XeCH_3^+$	aVDZ	−367.864964
	aVTZ	−128.812648		aVTZ	−42.309981		aVTZ	−367.968060
	aVQZ	−128.847460		aVQZ	−42.320770		aVQZ	−367.998305
	aV5Z	−128.859837		aV5Z	−42.323983		aV5Z	−368.007664
	CBS(eq 3)	−128.872823		CBS(eq 3)	−42.327354		CBS(eq 3)	−368.017483
	CBS(eq 1)	−128.867415		CBS(eq 1)	−42.326444		CBS(eq 1)	−368.015178
Ar	aVDZ	−526.969685	$NeCH_3^+$	aVDZ	−168.084855			
	aVTZ	−527.048758		aVTZ	−168.223700			
	aVQZ	−527.075055		aVQZ	−168.267282			
	aV5Z	−527.083436		aV5Z	−168.282044			
	CBS(eq 3)	−527.092229		CBS(eq 3)	−168.297532			
	CBS(eq 1)	−527.090009		CBS(eq 1)	−168.291934			

[a] CBS values for eq 1 obtained with the aug-cc-pVnZ basis sets with n = D, T, Q. CBS values for eq 3 obtained with the aug-cc-pVnZ basis sets with n = Q, 5.

valence (CV) calculations were carried out with the weighted core-valence basis sets, i.e., cc-pwCVnZ, or their diffuse function augmented counterparts, aug-cc-pwCVnZ,[37] at the triple-ζ level. For Xe, the cc-pwCVTZ basis set contains up through g-functions in order to provide a consistent degree of angular correlation for the active 4d electrons. The cc-pwCVTZ (or aug-cc-pwCVTZ) basis set for Xe is based on the cc-pVTZ-PP (aug-cc-pVTZ-PP) basis set and accompanying small core RECP. Core/valence calculations for Xe involve all 26 electrons outside the RECP core, i.e., $4s^2$, $4p^6$, $5s^2$, $4d^{10}$, and $5p^{6.}$

We account for molecular scalar relativistic effects, ΔE_{SR}, in the methyl cation affinity by using expectation values for the two dominant terms in the Breit−Pauli Hamiltonian, the so-called mass-velocity and one-electron Darwin (MVD) corrections from configuration interaction singles and doubles (CISD) calculations. ΔE_{SR} was obtained from CISD wave functions with an aVTZ basis set at the CCSD(T)/aVTZ geometry. The CISD(MVD) approach generally yields ΔE_{SR} values in good agreement (±0.3 kcal/mol) with more accurate values for $\sum D_0$ for most molecules. A potential problem arises in computing the scalar relativistic correction for the molecules in this study as there is the possibility of "double counting" the relativistic effect on Xe when applying a MVD correction to an energy that already includes most relativistic effects via the RECP. Because the MVD operators mainly sample the core region where the pseudoorbitals are small, we assume any double counting to be small.

Geometry optimizations were performed with a convergence threshold on the gradient of approximately 10^{-4} E_h/bohr or smaller. Geometries were optimized at the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ levels for the rare gas−methyl cation complexes at the CCSD(T) level. The CCSD(T)/aug-cc-pVQZ geometry was used for the CCSD(T)/aug-cc-pV5Z energy calculations for the rare gas−methyl cation affinities. For N_2, CH_2N_2, and $CH_3N_2^+$, the geometries were optimized at the CCSD(T) level with the aug-cc-pVDZ and aug-cc-pVTZ basis sets. The CCSD(T)/aug-cc-pVTZ geometry was used for the CCSD(T)/aug-cc-pVQZ energy calculations for N_2, $CH_3N_2^+$, and CH_2N_2.

To convert vibrationless atomization energies, $\sum D_e$, to $\sum D_0^0$, and ultimately to $\Delta H_f^{\,0}$ and ΔH_f^{298}, we require as accurate molecular zero-point vibrational energy corrections, ΔE_{ZPE}, as possible. For the polyatomic molecules, we calculated the frequencies at the CCSD(T) level with the aug-cc-pVDZ basis set and averaged these values with the experimental ones to estimate the anharmonic zero-point energy following the suggestion of Grev et al.[38]

To calculate the heat of formation of CH_2N_2 by calculating $\sum D_0$, we need to calculate the energies of the C and N atoms which are open shells. Of the three reported coupled cluster approaches to handling open shell systems, we have chosen to use the restricted method for the Hartree−Fock wave function with relaxation of the spin restriction in the coupled cluster portion of the calculation. This method is conventionally labeled R/UCCSD(T). In addition to the ΔE_{SR} contribution to $\sum D_0$(CH_2N_2), we also need to replace atomic energies that correspond to an average over the available spin multiplets with energies for the lowest multiplets as most electronic structure codes are only capable of producing spin multiplet averaged wave functions. The atomic spin−orbit correction of 0.08 for C is from the tables of Moore.[39] By combining our computed $\sum D_0$ values with the known[40] heats of formation at 0 K for the elements [$\Delta H_f^0(N) = 112.53 \pm 0.02$ kcal mol^{-1}, $\Delta H_f^0(H) = 51.63$ kcal mol^{-1}, and $\Delta H_f^0(C) = 169.98 \pm 0.1$ kcal mol^{-1}] we can derive ΔH_f^0 for CH_2N_2.

Results and Discussion

Rare Gas−Methyl Cation Affinities. The total energies used in this study are given in Table 1. The geometries for CH_3^+ and the rare gas compounds are given in Table 2. The calculated harmonic frequencies are given in Table 3. The energetic contributions to the calculation of the methyl cation affinities are given in Table 4.

The geometries show interesting variations with basis set. The C−Rg bond length always gets significantly shorter with increasing size of the basis set. This is most visible for the weakest interaction, CH_3^+ with He, where the bond distance

TABLE 2: CCSD(T) Geometry Parameters for Rare Gas (Rg)−Methyl Cation Clusters[e]

molecule	basis set	r(C−H)	R(C−Rg)	∠HCRg
CH_3^+(D_{3h})	aVDZ	1.1035		
	aVTZ	1.0907		
	aVQZ	1.0893		
	expt[a]	1.087		
$HeCH_3^+$	aVDZ	1.1027	2.0236	90.68
	aVTZ	1.0890	1.8385	91.39
	aVQZ	1.0876	1.8215	91.48
	expt[b]		2.176	
$NeCH_3^+$	aVDZ	1.1020	2.2158	91.00
	aVTZ	1.0888	2.1471	91.26
	aVQZ	1.0872	2.1300	91.30
	expt[c]		2.300	
$ArCH_3^+$	aVDZ	1.0982	2.0838	97.10
	aVTZ	1.0850	2.0081	98.61
	aVQZ	1.0836	2.0003	98.66
	expt[d]		2.018/2.053	
$KrCH_3^+$	aVDZ	1.0978	2.1415	99.35
	aVTZ	1.0847	2.0863	100.50
	aVQZ	1.0835	2.0846	100.47
$XeCH_3^+$	aVDZ	1.0977	2.2642	101.55
	aVTZ	1.0848	2.2168	102.26
	aVQZ	1.0837	2.2165	102.21

[a] Crofton, M. W.; Jagod, M.-F.; Rehfuss, B. D.; Kreiner, W. A.; Oka, T. *J. Chem. Phys.* **1988**, *88*, 666. [b] Reference 16. [c] Reference 17. [d] Reference 18. [e] Bond distances in Å and bond angles in deg.

decreases by almost 0.20 Å going from the aVDZ to the aVQZ basis set. The He−C distance is 1.82 Å and there is a significant lengthening to 2.13 Å for Rg = Ne. As the interaction energy significantly increases (see below) from Rg = Ar, the C−Ar bond length is actually shorter at 2.00 Å as is the C−Kr bind distance at 2.08 Å. The Xe−C distance increases and is the longest at 2.22 Å. The C−H bond distances all decrease slightly from the free ion on binding to the rare gas. The experimental Rg−C distances determined as $R_{C.M.}$ for Rg = He and Ne are much longer than the calculated Rg−C distances as observed previously.[16−19] This has been interpreted as being due to large-amplitude zero-point motions in the ground vibrational state. The ∠HCRg is coupled to this distance at the aVDZ and aVTZ levels. As the C−Rg distance decreases, this angle becomes larger, i.e., the CH_3^+ deviates more from planarity. This angle increases as the strength of the interaction increases from 91.5° for Rg = He to 102.2° for Rg = Xe. There is a big jump between Ne and Ar in this angle parameter.

The C−H stretching frequencies are only weakly perturbed by binding to the rare gas as are the degenerate HCH bending frequencies. The C−H asymmetric stretch has been shown to blue shift on complexation to a rare gas and the calculated values show exactly the same trends as the experimental values.[16−19] The symmetric CH_3 inversion mode is sensitive to the addition of the rare gas decreasing from the frequency of 1428 cm^{-1} in the free cation to 1270 cm^{-1} for Rg = Xe. There is little perturbation of this mode for Rg = He or Ne. The C−Rg stretch increases from 156 cm^{-1} for Rg = Ne to 173 cm^{-1} for Rg = He due to a mass effect. The largest value for this mode is for Rg = Xe with a value of 392 cm^{-1} even though Xe is the heaviest rare gas. The degenerate HCRg bend is also sensitive to the rare gas with the strength of the interaction ranging from 422 cm^{-1}, for Rg = Ne, to 927 cm^{-1}, for Rg = Kr.

The various terms in calculating the methyl cation affinities (MCAs) are given in Table 4. The methyl cation affinity is defined as the negative of the energy of reaction 4.

$$CH_3^+ + Rg \rightarrow RgCH_3^+ \qquad (4)$$

TABLE 3: CCSD(T)/Aug-cc-pVDZ Frequencies (in cm^{-1}) for Rare Gas (Rg)−Methyl Cation

molecule	calcd[a]	expt	assignment
CH_3^+	3246(e)	3108.4[b]	C−H stretch
	3036(a)		C−H stretch
	1428(a)	1380(20)[b]	CH_3 inversion
	1417(e)		HCH bend
$HeCH_3^+$	3254(e)	3115[c]	C−H stretch
	3043(a)		C−H stretch
	1416(e)		HCH bend
	1415(a)		CH_3 inversion
	428(e)		He−C bend
	173(a)		He−C stretch
$NeCH_3^+$	3259(e)	3119[d]	C−H stretch
	3048(a)		C−H stretch
	1417(e)		HCH bend
	1410(a)		CH_3 inversion
	422(e)		Ne−C bend
	156(a)		Ne−C stretch
$ArCH_3^+$	3274(e)	3145(30)[e]	C−H stretch
	3077(a)		C−H stretch
	1416(e)		HCH bend
	1342(a)		CH_3 inversion
	890(e)		Ar−C bend
	311(a)		Ar−C stretch
$KrCH_3^+$	3264(e)		C−H stretch
	3078(a)		C−H stretch
	1415(e)		HCH bend
	1308(a)		CH_3 inversion
	927(e)		Kr−C bend
	352(a)		Kr−C stretch
$XeCH_3^+$	3251(e)		C−H stretch
	3078(a)		C−H stretch
	1416(e)		HCH bend
	1270(a)		CH_3 inversion
	917(e)		Xe−C bend
	392(a)		Xe−C stretch

[a] Symmetry labels given after calculated values in parentheses. [b] Crofton, M. W.; Jagod, M.-F.; Rehfuss, B. D.; Kreiner, W. A.; Oka, T. *J. Chem. Phys.* **1988**, *88*, 666. Dyke, J. Jonathan, N.; Lee, E.; Morris, A. *J. Chem. Soc.*, *Faraday Trans. 2* **1976**, *72*, 1385. [c] Reference 16. [d] Reference 17. [e] Reference 18.

The difference between the complete basis set valence electronic energies obtained with eq 1 and eq 3 ranges from ∼0 for He to 1.06 kcal/mol for Xe. To obtain our best estimate for the valence correlation contribution, we averaged the two CBS estimates in our calculation of the MCAs for the rare gases. The largest correction term is the zero-point energy difference, which increases with increasing binding energy. The other correction terms are small. The methyl cation affinities (MCA) of the rare gases are very small for Rg = He and Ne being 0.9 and 1.7 kcal/mol at 0 K, respectively. There is a big jump to 16.0 kcal/mol for Rg = Ar. The value for Rg = Kr is larger at 24.3 kcal/mol and the largest value is 35.9 kcal/mol for Rg = Xe.

To compare the calculated values to experiment, the original experimental methyl cation affinities for Xe and Kr have to be corrected based on the new scale derived by McMahon, Radom, and co-workers.[27] This places the $MCA^{298}(N_2)$ at 44.0 kcal/mol. The experimental value for the MCA^{298}(Xe) is 2.5 kcal/mol above that of N_2 giving $MCA^{298}(Xe) = 46.5 \pm 3$ kcal/mol. The experimental value for MCA(Kr) is 4.4 kcal/mol below that of N_2 giving $MCA^{298}(Kr) = 39.6$ kcal/mol. The calculated and experimental MCA's at 298 K are compared in Table 5. Our calculated MCA^{298}(Xe) is 36.6 kcal/mol, 10 kcal/mol below either experimental value.[13,15] One experimental value for MCA^{298}(Kr) is almost 14 kcal/mol larger[13] than our calculated value of $MCA^{298}(Kr) = 25.5$ kcal/mol and the other experimental value[15] for MCA^{298}(Kr) is 6 kcal/mol below our calculated value. There is a clear discrepancy between our

TABLE 4: Calculated Methyl Cation Affinities (MCAs)[a]

molecule	ΔE_{elec}(CBS)[b] eq 1	ΔE_{elec}(CBS)[c] eq 3	ΔE_{elec}(CBS)[d] av	ΔE_{ZPE}[e]	ΔE_{CV}[f]	ΔE_{SR}[g]	D_e(av)[h]	MCA(0 K)[i] av
$\mathrm{HeCH_3^+}$	2.37	2.36	2.36	−1.45	0.01	0.00	2.37	0.92
$\mathrm{NeCH_3^+}$	3.26	3.15	3.20	−1.43	0.00	−0.03	3.17	1.74
$\mathrm{ArCH_3^+}$	18.24	18.68	18.46	−2.94	0.26	0.01	18.73	15.79
$\mathrm{KrCH_3^+}$	26.85	27.34	27.10	−3.03	0.27	−0.04	27.33	24.30
$\mathrm{XeCH_3^+}$	38.44	39.50	38.97	−3.97	0.44	−0.05	39.36	35.39

[a] Results are given in kcal/mol. [b] Extrapolated by using eq 1 with aD, T, Q. [c] Extrapolated by using eq 3 with aQ, 5. [d] Average of ΔE_{elec}(CBS) from eqs 1 and 3. [e] Zero-point energy difference ZPE($\mathrm{RgCH_3^+}$) − ZPE($\mathrm{CH_3^+}$) at the CCSD(T)/aug-cc-pVDZ level. [f] Core/valence corrections were obtained at the CCSD(T)/aug-cc-pwCVTZ level at the optimized CCSD(T)/aug-cc-pVTZ geometries. [g] The scalar relativistic correction is based on a CISD(FC)/aug-cc-pVTZ-PP/aug-cc-pVTZ MVD calculation and is expressed relative to the CISD result without the MVD correction, i.e., including the existing relativistic effects resulting from the use of a relativistic effective core potential. [h] D_e for the Rg−C bond to the products $\mathrm{CH_3^+}$ + Rg in the complex including all corrections except ΔZPE. [i] The MCA(0 K) was computed with the average CBS estimate.

TABLE 5: Calculated and Experimental MCAs at 298 K (in kcal/mol)

rare gas	calcd (this work)[a]	expt 1[a]	expt 2[b]	calcd[c]
He	1.7			1.1
Ne	2.5		1.2 ± 0.3	2.5
Ar	16.9		11.3	17.2
Kr	25.5	39.6	19.8 ± 2.0	25.5
Xe	36.6	46.5 ± 3	46.1 ± 0.6	39.0

[a] We estimate that our calculated MCA values for He, Ne, and Ar have error bars of ±0.5 kcal/mol, ±0.75 kcal/mol for Kr, and ±1.0 kcal/mol for Xe. [b] Reference 13. [c] Reference 15. For He, Ne, Ar, and Kr, the results are at the G2MP2 level. The MCA(Xe) is at the B3LYP/DZVP level. The QCISD(T)(full)/6-311++G(2df,p) values for the MCA's of He, Ne, Ar, and Kr are 0.6, 2.5, 15.8, and 24.2 kcal/mol, respectively.

calculated value and the experimental values and between the two experimental values. The calculated MCA[29] value for Ne of 2.5 kcal/mol is in reasonable agreement with the experimental value of 1.2 kcal/mol. The calculated value for Rg = Ar of 17.5 kcal/mol at 298 K is 6 kcal/mol higher than the experimental value, the same difference as found for MCA(Kr). The current calculated values are in reasonable agreement with the calculated values at the QCISD(T) level with smaller basis sets for the MCA of He, Ne, Ar, and Kr within less than 2 kcal/mol.[15] The G2MP2 values for the MCA's of He through Kr are in excellent agreement with our much higher level results. Even for MCA(Xe), the B3LYP/DZVP result[15] is in reasonable agreement with our CCSD(T) result and closer to it than to the experimental values. The calculated D_e values reported at the MP2 level with a modified aug-cc-pVTZ basis set of 2.02,[16] 2.74,[17] and 15.93[18] kcal/mol can be compared to our values of 2.37, 3.17, and 18.73 kcal/mol. The differences are due to a combination of correlation energy treatment and basis set effects.

To compare the methyl cation affinities with the proton affinities, we calculated the proton affinities in the same way as the MCAs. We provide a summary of the proton affinities in Table 6 and the quantities used to compute them. The zero-point energies were calculated from ω_e and $\omega_e x_e$ obtained at the CCSD(T)/aug-cc-pVQZ-PP level with 5th degree Dunham fit[41] of the potential energy surface. The calculated value for $D_e(\mathrm{HeH^+})$ of 47.08 kcal/mol is in excellent agreement with the value of 47.02 kcal/mol obtained by Kolos and Peek based on an 83-term variational wave function in elliptic coordinates.[42] Our calculation of this 2 electron system is a full CI extrapolated to the complete basis set limit. Thus our value is to be preferred over the "experimental" value taken from Hunter and Lias,[43] which was originally obtained from this value. For Ne and Ar, the experimental proton affinities[43] are not well-established so the values we provide are the most accurate available. For $\mathrm{KrH^+}$, we calculate a proton affinity of 102.2 kcal/mol, which is 0.7 kcal/mol above the experimental value of 101.5 kcal/mol at 298 K. For $\mathrm{XeH^+}$, we calculate a proton affinity of 117.6 kcal/mol at 298 K, which is 1.8 kcal/mol below the experimental value of 119.4 kcal/mol. Again, we prefer our calculated value to those tabulated by Hunter and Lias[43] and note that it has been extremely difficult to measure such low proton affinities due to the lack of molecules with such low values needed to generate an overlapped scale. We note that our values for ΔE_{elec} for $\mathrm{KrH^+}$ and $\mathrm{XeH^+}$ are essentially identical with those in ref 26.

The proton affinities for He and Ne are low and similar to each other just as found for the MCA values. There is a substantial jump from these values to PA(Ar) and the PA for Kr is higher by about 11 kcal/mol as compared to that for Ar and that from Xe is about 15 kcal/mol higher than that for Kr. Thus the PA's exhibit the same trends as our calculated rare gas MCA's as expected.

Potential components of the weak interactions describing the binding of $\mathrm{CH_3^+}$ to a rare gas are the atomic polarizabilities. These quantities for Kr and Xe have been previously calculated[26] by using identical methods as the present work and were found to be in very good agreement with experiment. At the CCSD(T)/aug-cc-pV5Z-PP level, the value for α(Kr) is 16.93 au as

TABLE 6: Calculated Proton Affinities (PA, in kcal/mol)

molecule	ΔE_{elec}(CBS)[a] eq 3	ΔE_{ZPE}[b]	ΔE_{CV}[c]	ΔE_{SR}[d]	PA(0 K) calcd	PA(298 K) calcd	PA(298 K) expt[43]
$\mathrm{HeH^+}$	47.08	−4.48		0.00	42.60	43.5	42.5
$\mathrm{NeH^+}$	52.85	−4.09	−0.04	−0.04	48.68	49.6	47.5
$\mathrm{ArH^+}$	93.99	−3.84	0.04	0.06	90.25	91.1	88.2
$\mathrm{KrH^+}$	105.03	−3.54	−0.15		101.34	102.2	101.5
$\mathrm{XeH^+}$	120.32	−3.24	−0.33		116.75	117.6	119.4

[a] Extrapolated by using eq 3 with aQ, 5. [b] Zero-point energy difference calculated as $0.5\omega_e - 0.25\omega_e x_e$ at the CCSD(T)/aug-cc-pVQZ level. [c] Core/valence corrections were obtained at the CCSD(T)/aug-cc-pwCVTZ level at the optimized CCSD(T)/aug-cc-pVTZ geometries. [d] The scalar relativistic correction is based on a CISD(FC)/aug-cc-pVTZ MVD calculation. As there are no additional electrons on $\mathrm{H^+}$ and the fact that we included scalar relativistic terms in the effective core potential for Kr and Xe, there is no additional contribution to the PA calculations for these atoms.

TABLE 7: Calculated Geometry Parameters for N_2, CH_2N_2, and $CH_3N_2^+$ [c]

molecule	basis set	r_e(C−H)	r_e(C−N)	r_e(N−N)	∠HCN
N_2	aVDZ			1.1209	
	aVTZ			1.1040	
	expt[a]			1.09768	
$N_2CH_3^+$	aVDZ	1.0996	1.6806	1.1183	94.49
	aVTZ	1.0897	1.4733	1.1019	105.68
CH_2N_2	aVDZ	1.0888	1.3165	1.1592	117.35
	aVTZ	1.0760	1.3030	1.1434	117.36
	expt[b]	1.075	1.300	1.140	117.0

[a] Reference 47. [b] Reference 46. [c] Bond angles in Å and bond angles in deg.

compared to an experimental value[44] of 16.79 au and the value for α(Xe) is 27.44 au as compared to an experimental value of 27.16 au.

To account for other effects that might explain the difference between the calculated and experimental values for MCA(Xe), we performed a second-order spin−orbit calculation for Xe-CH_3^+. The lowest spin−orbit coupled eigenstates were obtained by diagonalizing relatively small spin−orbit matrixes (6 singlets and 5 triplets) in a basis of pure spin (Λ−S) eigenstates at the CASSCF level using the SO parameters from the RECP. The ground-state energy of $XeCH_3^+$ was lowered by 2nd order SO coupling by about 0.4 kcal/mol. Thus, this effect cannot explain the difference between experiment and theory for the MCA-(Xe). These calculations also showed that multireference character is not important in the ground state of $XeCH_3^+$ as the lowest excited state is already nearly 6 eV above the ground state. The T_1 diagnostic[45] for the CCSD calculation on $XeCH_3^+$ has a value of just 0.012 with the aug-cc-pVQZ basis set, consistent with a ground state dominated by a single configuration. Cunje et al.[15] performed a B3LYP calculation for MCA-(Xe) with the DZVP basis set, which has angular momentum functions up through d functions. They suggested that back charge transfer from CH_3^+ to the Xe 4f orbital could explain the difference between their calculated value and the experimental one. Our calculations which include these contributions (we have basis sets with angular momentum functions up through h functions) show that this back-bonding argument cannot explain the difference between theory and experiment. Even if we take the value of D_e(Xe−CH_3^+) from the CBS extrapolation using eq 3, this would increase our calculated MCA by only 0.53 kcal/mol, which is not enough to change the agreement with the experimental value. We note that the valence CCSD(T) electronic contribution to MCA($XeCH_3^+$) with the aug-cc-pV5Z basis set is 39.46 kcal/mol, within 0.04 kcal/mol of the extrapolated value using eq 3.

Diazomethane. The calculated geometries for diazomethane and $CH_3N_2^+$ are given in Table 7, the calculated frequencies in Table 8, the total energies in Table 9, and the energy components for calculating the heat of formation of CH_2N_2, its proton affinity, and MCA(N_2) in Table 10.

TABLE 8: Calculated Frequencies for N_2, CH_2N_2, and $N_2CH_3^+$ (in cm^{-1})

molecule	calcd	expt[a]	assignment
N_2	2319.1	2331 (2358.6)[b]	NN stretch
CH_2N_2	3336.6	3188	b_2 C−H asym stretch
	3194.4	3077	a_1 C−H sym stretch
	2109.8	2102	a_1 NN stretch
	1425.7	1414	a_1 δ CH_2
	1168.3	1170	a_1 CN stretch
	1101.9	1109	b_2 CH_2 rock
	536.2	564	b_1 δ CNN out of plane
	386.1	421	b_2 δ CNN in plane
	298.3	406	b_1 CH_2 wag
$N_2CH_3^+$	3245.8		e C−H stretch
	3057.4		a_1 C−H stretch
	2334.4		a_1 NN stretch
	1419.4		e HCH bend
	1338.7		a_1 CH_3 inversion
	1147.9		e bend
	314.5		a_1 C−N stretch
	279.1		e bend

[a] Reference 47 for N_2 and ref 48 for CH_2N_2. [b] Harmonic value in parentheses.

TABLE 9: Total Energies (E_h) for N_2, CH_2N_2, and $N_2CH_3^+$ [a]

system	basis set	energy
N_2	aVDZ	−109.2953201
	aVTZ	−109.3808451
	aVQZ	−109.4072432
	CBS(eq 1)	−109.422126
CH_2N_2	aVDZ	−148.3835508
	aVTZ	−148.5093657
	aVQZ	−148.5458840
	CBS(eq 1)	−148.566211
$CH_3N_2^+$	aVDZ	−148.7145574
	aVTZ	−148.8599699
	aVQZ	−148.8955580
	CBS(eq 1)	−148.914572

[a] CBS values for eq 1 obtained with the aug-cc-pVnZ basis sets with n = D, T, Q.

TABLE 10: Components for Calculating ΔH_f(CH_2N_2), PA(CH_2N_2), and MCA(N_2) (in kcal/mol)[a]

	CBS eq 1[b]	ΔE_{ZPE}[c]	ΔE_{CV}[d]	ΔE_{SR}[e]	ΔE_{SO}[f]	$\sum D_0$(0 K)[g]
ΔH_f(CH_2N_2)	449.59	−19.42	2.03	−0.51	−0.08	431.61
PA(CH_2N_2)	218.60	−7.76	−0.31	0.13	0.0	210.66
MCA(N_2)	45.96	−4.42	0.55	−0.15	0.0	41.94

[a] The proton affinity reaction is $CH_3N_2^+ \rightarrow CH_2N_2 + H^+$. The methyl cation affinity reaction is $CH_3N_2^+$ ‡ $N_2 + CH_3^+$. Results are given in kcal/mol. [b] Extrapolated by using eq 1 with aD, T, Q. [c] Zero-point energy differences based on CCSD(T)/aug-cc-pVDZ level frequencies appropriately scaled. See text. [d] Core/valence corrections were obtained at the CCSD(T)/aug-cc-pwCVTZ level at the optimized CCSD(T)/aug-cc-pVTZ geometries. [e] The scalar relativistic correction is based on a CISD/cc-pVTZ MVD calculation. [f] Spin−orbit correction taken from ref 39. [g] Atomization energy for CH_2N_2, 1st value, PA(CH_2N_2), 2nd value, and MCA(N_2), 3rd value.

The geometry for diazomethane is in excellent agreement with the available experimental values[46] as is the geometry for N_2.[47] The addition of the proton to CH_2N_2 to form $CH_3N_2^+$ leads to a significant lengthening of the C−N bond. Again, as found for the other CH_3^+ complexes, there is a significant dependence on the basis set for the geometry of $CH_3N_2^+$.

The N_2 stretch is calculated to be too low by 40 cm^{-1} as compared to the experimental harmonic value.[47] The CH stretches in CH_2N_2 are calculated to be too high in comparison to experiment as expected.[48] The calculated harmonic NN and CN stretches are within a few wavenumbers of the experimental values as are the a_1 δ CH_2 and b_2 CH_2 rock bending modes. The calculated values for the lowest three modes are below the experimental values with the largest error of almost 100 cm^{-1} found for the lowest mode, the b_1 CH_2 wag. We can estimate the zero-point energy by averaging the CCSD(T) and experimental values for the four highest modes and then using the experimental values for the lower energy modes. The use of the four highest modes yields a scale factor for the average of 0.986 that we can use for the calculation of the $CH_3N_2^+$ ZPE. We used a similar scaling procedure for CH_3^+ for calculating MCA(N_2) for consistency. The NN stretch in $CH_3N_2^+$ is predicted to be greater than that in N_2. The C−N stretch in $CH_3N_2^+$ is predicted to be lower than the C−Xe and C−Kr stretches in CH_3Xe^+ and CH_3Kr^+.

The heat of formation of CH_2N_2 is calculated to be 66.7 kcal/mol at 0 K and 65.3 kcal/mol at 298 K. This is significantly larger than the lower limit of 51.3 kcal/mol based on a photodissociation method.[29] It also differs significantly from early appearance potential studies based on electron impact experiments which gave 49.3 ± 2.3 kcal/mol.[49] The calculated value is in reasonably good agreement with the value of $\Delta H_f(CH_2N_2) > 67$ kcal/mol predicted by Setser and Rabinovitch based on RRKM calculations of thermally activated methylene−olefin reactions.[50] The heat of formation of CH_2N_2 has been reported at the G2 level based on an atomization energy as 64.3 kcal/mol at 298 K and as 63.1 kcal/mol based on G2 calculations of isodesmic reactions averaged with the atomization energy.[30] The G2 heat of formation of CH_2N_2 is in reasonable agreement with our value of 65.3 kcal/mol obtained at a higher level but the average value is not as good.

The proton affinity of CH_2N_2 is calculated to be 210.7 kcal/mol at 0 K and 211.9 kcal/mol at 298 K. This is in good agreement with the G2 calculated value[13] of 211.2 kcal/mol but not with the current experimental value of 205.3 kcal/mol.[43] The calculated value for MCA(N_2) at 0 K is 41.9 and 43.2 kcal/mol at 298 K in excellent agreement with the G2 value of 42.9 and the revised experimental value of 44.0 kcal/mol.[13]

Conclusion

A composite CCSD(T)-based approach was used to compute geometries, normal-mode frequencies, and the methyl cation affinities (MCA's) of the rare gases. These calculated values are currently the most reliable values available for these species. The methyl cation is very weakly bound to He and Ne and is more strongly bound to the heavier rare gases with the MCA increasing by 9 kcal/mol from Ar to Kr and by 10 kcal/mol from Kr to Xe. The MCA's from experiment are not in agreement with the theoretical values, which is surprising as the calculated values should be highly reliable and should be accurate to ±1 kcal/mol. There are no obvious reasons for the discrepancy between the experimental and calculated values. Possible reasons for the discrepancy include the potential that there are other geometries involved for $N_2CH_3^+$ and $XeCH_3^+$ which are important in the experimental measurements and that the observed transfer process is dependent on the way in which the ions are generated. Although this possibility is unlikely based on a quick scan of potential geometries that we have performed, it needs to be investigated in more detail and we will pursue this in a separate publication. We note that the available theoretical values are in general agreement with each other.

As part of this study, we also calculated MCA(N_2) and find it to be in excellent agreement with the experimental value. We also suggest a revision of PA(CH_2N_2) to a higher value consistent with that of previous workers.[13] The calculated value for $\Delta H_f(CH_2N_2) = 65.3$ kcal/mol shows that there is a need to substantially revise the heat of formation for diazomethane to a more positive value from the currently accepted values[51] near 50 kcal/mol.

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